comparable to the 3·15 and 3·11 Å distances found in the N···C contacts in *m*- and *p*-$C_6Cl_4(CN)_2$ (Britton, 1981*a*). In the chlorine compound that is most directly analogous to this one, namely *o*-$C_6Cl_4(CN)_2$, the molecules pack in planar layers where all of the short contacts are between N and Cl atoms (Britton, 1981*b*).

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Structure of 3-*O*-Acetylgibberellin A_3

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Abstract. $C_{21}H_{24}O_7$, $M_r = 388{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}279\ (10)$, $b = 15{\cdot}615\ (10)$, $c = 9{\cdot}427\ (8)$ Å, $V = 1954{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}319$ g cm^{-3}, $\lambda(\text{Mo}\ K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}0$ cm^{-1}, $F(000) = 824$, $T = 293$ K, $R = 0{\cdot}049$ for 1805 observed reflections. The gibberellane skeleton shows the conformational variety characteristic of many other gibberellin derivatives. Ring *A* is in a sofa conformation while the five-membered ring *B* assumes an intermediate conformation between an envelope and a half-chair. The lactone ring is in an ideal envelope conformation and shows a marked difference in its two C—O distances. Each molecule is hydrogen bonded to two others to form continuous spiral chains along the *c* axis.

Introduction. The gibberellins are a large group of plant hormones isolated from culture filtrates of the fungus *Gibberella fujikuroi.* Among these active fungal metabolites, gibberellin A_3 (or gibberellic acid) is known to be the most important metabolite of the fungus *Gibberella fujikuroi* and has been the subject of exhaustive chemical studies (Curtis & Cross, 1954; Stork & Newman, 1959; Grove, 1961; Sheppard, 1960). All gibberellins are diterpenoid acids based on the tetracyclic gibberellane skeleton. The structure and absolute stereochemistry of gibberellin A_3 have been determined from X-ray studies of some of its derivatives (Hartsuck & Lipscomb, 1963; McCapra, McPhail, Scott, Sim & Young, 1966). During the course of our continuing investigation of natural products from marine organisms, we encountered an extract from the marine boring sponge *Cliona cariboea* which was later identified as a gibberellin derivative, 3-*O*-acetylgibberellin A_3. The crystal structure was carried out to characterize the compound fully.

Experimental. Thick platy crystals grown from methanol solution, $0{\cdot}90 \times 0{\cdot}35 \times 0{\cdot}12$ mm; space group from systematic absences; CAD-4 single-crystal X-ray diffractometer, Mo $K\bar{\alpha}$ radiation (graphite monochromator), lattice parameters from setting of 48 reflections with $9 < \theta < 13°$. 2311 unique reflections with $2\theta \le 53°$; $0 \le h \le 14$, $0 \le k \le 15$, $0 \le l \le 11$; θ–2θ scan, scan width $(0{\cdot}80 + 0{\cdot}20\tan\theta)°$, extended 25% on each side for background measurement, horizontal aperture $(3{\cdot}0 + 0{\cdot}86\tan\theta)$ mm, vertical

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Table 1. *Atomic parameters; e.s.d.'s are within parentheses*

	x	y	z	U_{eq}*(Å^2)
O(1)	0·8566 (3)	0·6397 (3)	−0·2270 (4)	0·080 (1)
O(2)	0·7812 (2)	0·5674 (2)	−0·0531 (3)	0·0496 (9)
O(3)	0·5049 (2)	0·5857 (2)	−0·3219 (4)	0·074 (1)
O(4)	0·4953 (2)	0·4635 (2)	−0·2018 (3)	0·0452 (9)
O(5)	0·3754 (3)	0·6227 (2)	0·2345 (4)	0·062 (1)
O(6)	0·5259 (2)	0·5732 (3)	0·2942 (4)	0·081 (1)
O(7)	0·1487 (2)	0·3392 (2)	0·0175 (3)	0·0438 (9)
C(1)	0·6419 (3)	0·3884 (3)	−0·1116 (4)	0·044 (1)
C(2)	0·7160 (3)	0·4393 (3)	−0·1511 (5)	0·058 (2)
C(3)	0·7059 (3)	0·5352 (3)	−0·1510 (5)	0·049 (1)
C(4)	0·6005 (3)	0·5680 (2)	−0·1032 (5)	0·044 (1)
C(5)	0·5596 (3)	0·5101 (2)	0·0138 (4)	0·034 (1)
C(6)	0·4540 (3)	0·5305 (2)	0·0717 (4)	0·036 (1)
C(7)	0·4579 (3)	0·5776 (2)	0·2124 (4)	0·045 (1)
C(8)	0·3958 (2)	0·4428 (2)	0·0816 (4)	0·035 (1)
C(9)	0·4666 (3)	0·3760 (2)	0·0085 (5)	0·039 (1)
C(10)	0·5437 (3)	0·4278 (2)	−0·0694 (4)	0·039 (1)
C(11)	0·4101 (3)	0·3110 (3)	−0·0847 (6)	0·059 (2)
C(12)	0·3130 (3)	0·2813 (3)	−0·0170 (6)	0·048 (1)
C(13)	0·2522 (2)	0·3544 (2)	0·0526 (4)	0·038 (1)
C(14)	0·2933 (3)	0·4419 (2)	0·0070 (4)	0·035 (1)
C(15)	0·3658 (3)	0·4119 (3)	0·2319 (4)	0·048 (1)
C(16)	0·2724 (3)	0·3575 (2)	0·2116 (4)	0·041 (1)
C(17)	0·2169 (4)	0·3231 (3)	0·3102 (5)	0·057 (2)
C(18)	0·6005 (4)	0·6638 (3)	−0·0728 (8)	0·066 (2)
C(19)	0·5291 (3)	0·5432 (3)	−0·2220 (5)	0·049 (1)
C(20)	0·8537 (3)	0·6167 (3)	−0·1049 (5)	0·051 (1)
C(21)	0·9316 (4)	0·6376 (5)	0·0033 (7)	0·080 (2)

* $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

aperture 4 mm; three standard reflections measured every 7200 s of X-ray exposure, maximum variation 5%; intensities scaled for monitor variations; 1805 observed reflections on the basis $I \geq 2\sigma(I)$; Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods using *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977), refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976); $\sum w(F_o - F_c)^2$ is minimized, where $w = 3{\cdot}1025/\sigma^2(F)$; all H atoms located from difference map and refined with isotropic temperature factors; final $R = 0{\cdot}049$, $wR = 0{\cdot}051$ for 1805 observed reflections; $(\Delta/\sigma)_{max} = 0{\cdot}10$; $S = 1{\cdot}6$ for 343 variables; highest peak in the final difference map 0·2 e Å^{-3}.* Atomic scattering factors from *SHELX*.

Discussion. The final atomic parameters of the non-H atoms are listed in Table 1. The atom-numbering scheme and ring designations of the molecule are shown in Fig. 1. Bond distances, bond angles for the entire molecule and endocyclic torsion angles for the five rings are listed in Table 2. A stereoview of a single molecule of 3-*O*-acetylgibberellin A$_3$ is shown in an *ORTEP* (Johnson, 1976) plot in Fig. 2.

Table 2. *Bond distances* (Å), *angles* (°) *and endocyclic torsion angles* (°)

E.s.d.'s are within parentheses.

C(1)–C(2)	1·318 (6)	C(8)–C(15)	1·549 (5)
C(1)–C(10)	1·496 (5)	C(9)–C(10)	1·498 (5)
C(2)–C(3)	1·504 (7)	C(9)–C(11)	1·539 (6)
C(3)–C(4)	1·557 (6)	C(10)–O(4)	1·509 (4)
C(3)–O(2)	1·451 (5)	C(11)–C(12)	1·512 (7)
C(4)–C(5)	1·527 (5)	C(12)–C(13)	1·544 (6)
C(4)–C(18)	1·523 (6)	C(13)–C(14)	1·533 (5)
C(4)–C(19)	1·518 (6)	C(13)–O(7)	1·433 (4)
C(5)–C(6)	1·539 (5)	C(13)–C(16)	1·524 (5)
C(5)–C(10)	1·519 (5)	C(15)–C(16)	1·514 (6)
C(6)–C(7)	1·518 (6)	C(16)–C(17)	1·303 (6)
C(6)–C(8)	1·575 (5)	C(19)–O(3)	1·196 (6)
C(7)–O(5)	1·319 (5)	C(19)–O(4)	1·337 (5)
C(7)–O(6)	1·190 (5)	C(20)–O(2)	1·326 (5)
C(8)–C(9)	1·564 (5)	C(20)–O(1)	1·206 (6)
C(8)–C(14)	1·531 (5)	C(20)–C(21)	1·489 (7)

C(2)–C(1)–C(10)	118·5 (4)	C(8)–C(9)–C(10)	105·5 (3)
C(1)–C(2)–C(3)	122·3 (4)	C(8)–C(9)–C(11)	113·5 (3)
C(2)–C(3)–O(2)	106·5 (3)	C(10)–C(9)–C(11)	114·2 (4)
C(2)–C(3)–C(4)	114·1 (3)	C(1)–C(10)–C(5)	111·4 (3)
O(2)–C(3)–C(4)	108·7 (3)	C(1)–C(10)–C(9)	120·2 (3)
C(3)–O(2)–C(20)	117·8 (3)	C(1)–C(10)–O(4)	107·7 (3)
C(3)–C(4)–C(5)	109·5 (3)	C(5)–C(10)–O(4)	100·1 (3)
C(3)–C(4)–C(18)	112·2 (4)	C(5)–C(10)–C(9)	107·3 (3)
C(3)–C(4)–C(19)	105·3 (3)	O(4)–C(10)–C(9)	108·3 (3)
C(5)–C(4)–C(18)	116·5 (4)	C(9)–C(11)–C(12)	112·2 (4)
C(5)–C(4)–C(19)	99·1 (3)	C(11)–C(12)–C(13)	113·5 (4)
C(18)–C(4)–C(19)	112·9 (4)	C(12)–C(13)–C(14)	110·7 (3)
C(4)–C(5)–C(6)	117·2 (3)	C(12)–C(13)–O(7)	106·3 (3)
C(4)–C(5)–C(10)	100·2 (3)	C(14)–C(13)–O(7)	115·1 (3)
C(6)–C(5)–C(10)	103·4 (3)	C(14)–C(13)–C(16)	100·6 (3)
C(5)–C(6)–C(8)	106·8 (3)	O(7)–C(13)–C(16)	113·7 (3)
C(5)–C(6)–C(7)	112·3 (3)	C(13)–C(14)–C(8)	101·3 (3)
C(7)–C(6)–C(8)	112·8 (3)	C(8)–C(15)–C(16)	105·7 (3)
C(6)–C(7)–O(5)	111·7 (3)	C(13)–C(16)–C(15)	106·7 (3)
C(6)–C(7)–O(6)	124·3 (4)	C(13)–C(16)–C(17)	126·1 (4)
O(5)–C(7)–O(6)	124·0 (4)	C(15)–C(16)–C(17)	127·2 (4)
C(6)–C(8)–C(9)	105·0 (3)	C(4)–C(19)–O(3)	127·3 (4)
C(6)–C(8)–C(14)	114·7 (3)	C(4)–C(19)–O(4)	110·0 (3)
C(6)–C(8)–C(15)	116·8 (3)	O(2)–C(20)–O(1)	123·2 (4)
C(9)–C(8)–C(14)	109·0 (3)	O(1)–C(20)–C(21)	124·5 (4)
C(9)–C(8)–C(15)	110·5 (3)	O(2)–C(20)–C(21)	112·3 (4)
C(14)–C(8)–C(15)	100·8 (3)	C(12)–C(13)–C(16)	110·5 (3)
O(3)–C(19)–O(4)	122·7 (4)		

Ring *A*			
C(1)–C(2)–C(3)–C(4)	−1·1 (7)	C(4)–C(5)–C(10)–C(1)	69·4 (4)
C(2)–C(3)–C(4)–C(5)	36·2 (5)	C(5)–C(10)–C(1)–C(2)	−38·5 (5)
C(3)–C(4)–C(5)–C(10)	−67·0 (4)	C(10)–C(1)–C(2)–C(3)	1·8 (7)
Ring *B*			
C(5)–C(6)–C(8)–C(9)	−7·5 (4)	C(9)–C(10)–C(5)–C(6)	−35·7 (4)
C(6)–C(8)–C(9)–C(10)	−14·1 (4)	C(10)–C(5)–C(6)–C(8)	25·8 (4)
C(8)–C(9)–C(10)–C(5)	31·2 (4)		
Ring *C*			
C(8)–C(9)–C(11)–C(12)	−40·6 (5)	C(12)–C(13)–C(14)–C(8)	−68·8 (4)
C(9)–C(11)–C(12)–C(13)	42·5 (5)	C(13)–C(14)–C(8)–C(9)	69·8 (3)
C(11)–C(12)–C(13)–C(14)	12·8 (5)	C(14)–C(8)–C(9)–C(11)	−16·5 (5)
Ring *D*			
C(8)–C(14)–C(13)–C(16)	48·0 (3)	C(16)–C(15)–C(8)–C(14)	27·2 (4)
C(14)–C(13)–C(16)–C(15)	−30·8 (4)	C(15)–C(8)–C(14)–C(13)	−46·5 (3)
C(13)–C(16)–C(15)–C(8)	2·3 (4)		
Ring *E*			
O(4)–C(10)–C(5)–C(4)	−44·2 (3)	C(4)–C(19)–O(4)–C(10)	−1·4 (4)
C(10)–C(5)–C(4)–C(19)	42·9 (3)	C(19)–O(4)–C(10)–C(5)	29·1 (3)
C(5)–C(4)–C(19)–O(4)	−26·7 (4)		

Bond distances and bond angles are, in general, within the expected ranges and compare well with those observed in other related gibberellin derivatives. Slight

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44710 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lengthening of bonds C(3)—C(4) = 1·557 (6), C(6)—C(8) = 1·575 (5) and C(8)—C(9) = 1·564 (5) Å can be related to steric strain as substituents at all these atoms have β configuration. In the lactone ring, the distances C(19)—O(4) = 1·337 (5) and C(10)—O(4) = 1·509 (4) Å agree with the corresponding values of 1·345 and 1·492 Å observed in 3-dehydrogibberellin A_3 methyl ester (Kutschabsky, Reck, Hohne, Voigt & Adam, 1980) and 1·34 and 1·51 Å observed in 3-dehydrogibberellin A_3 (Kutschabsky, Reck & Adam, 1975).

The gibberellane skeleton shows the conformational variety characteristic of many other gibberellin derivatives. Ring *A* is in 5β-sofa conformation, with asymmetry parameter $\Delta C_s(5) = 2\cdot0^\circ$ [as defined by Duax & Norton (1975); $\Delta C_s = 0$ for an ideal sofa, $\Delta C_2 = 0$ for an ideal half-chair]. The five-membered ring *B* has an intermediate conformation between a 10α-envelope and 10α,5β-half-chair with asymmetric parameters $\Delta C_2(5\text{–}10) = 6\cdot0$ and $\Delta C_s(10) = 8\cdot9^\circ$. Ring *C* is in a boat conformation, while the five-membered ring *D* adopts an envelope conformation with atom C(14) as the flap. The γ-lactone ring is an almost ideal envelope [$\Delta C_s(5) = 1\cdot9^\circ$] with atom C(5) as the flap. The plane of the carboxylic acid group makes a dihedral angle of 68° with the plane defined by the atoms C(5), C(6) and C(8). Such a conformation of the 6β substituents is common to many other related structures (Ellames, Hanson, Hitchcock & Thomas, 1979; Kutschabsky, Reck & Adam, 1975; Fraga, Gonzalez, Hernandez, Tellado, Hanson & Hitchcock, 1981).

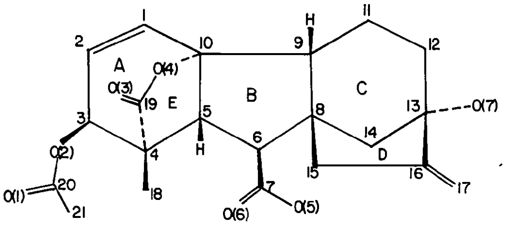

Fig. 1. A schematic of 3-*O*-acetylgibberellin A_3 showing the atom numbering and the absolute configuration.

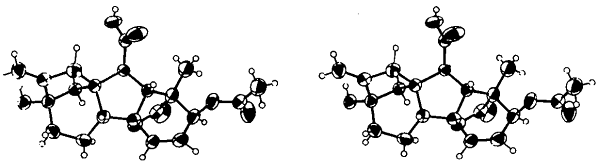

Fig. 2. A stereoview of the single molecule of 3-*O*-acetylgibberellin A_3.

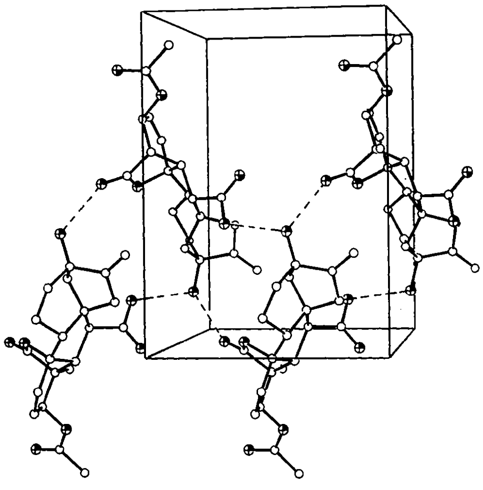

Fig. 3. A partial packing drawing showing the hydrogen bonding. *a* axis vertical; *c* axis horizontal.

Fig. 3 shows a partial packing scheme of the 3-*O*-acetylgibberellin A_3 structure. Each molecule forms two independent hydrogen bonds, O(7)—H···O(3) ($0\cdot5-x$, $1-y$, $0\cdot5+z$) = 2·798 (5) Å and O(5)—H···O(7) ($0\cdot5-x$, $1-y$, $0\cdot5-z$) = 2·752 (2) Å. Hydrogen-bonded molecules form continuous spiral chains along the *c* crystallographic axis.

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